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(54) Title: HYDROGENATION CATALYST AND METHOD FOR PREPARING TETRAHYDROFURAN

(57) Abstract

Hydrogenation in a back-mixed reactor or plug flow reactor of a hydrogenatable precursor such as maleic acid to tetrahydrofuran in the presence of a tri- or polymetallic catalytic composite consisting essentially of a combination of a catalytically effective amount of palladium, rhenium and one or more metals selected from rhodium, cobalt, platinum, ruthenium, iron, thulium, cerium, yttrium, neodymium, aluminum, praesodymium, holmium, copper, samarium, europium, hafnium, manganese, vanadium, chromium, gold, terbium, lutetium, nickel, scandium and niobium deposited on a support such as an activated, porous carbon carrier; and the continuous hydrogenation of a hydrogenatable precursor to tetrahydrofuran with hydrogen in a back mixed reactor in the presence of a suitable hydrogenation catalyst with continuous tetrahydrofuran removal while maintaining the concentration of acid within a predetermined range.

+ DESIGNATIONS OF "SU"

It is not yet known for which States of the former Soviet Union any designation of the Soviet Union has effect.

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TITLE

HYDROGENATION CATALYST AND METHOD
FOR PREPARING TETRAHYDROFURAN

CROSS-REFERENCE TO EARLIER FILED APPLICATION

This application is a continuation-in-part of application Serial No. 07/558,991, filed July 27, 1990.

BACKGROUND OF THE INVENTION
FIELD OF THE INVENTION

The present invention relates to the hydrogenation of hydrogenatable precursors to tetrahydrofuran in a back-mixed or a plug flow reactor in the presence of a novel tri- or polymetallic catalytic composite consisting essentially of a combination of: (1) a catalytically effective amount of palladium (Pd); (2) a catalytically effective amount of rhenium (Re); and, (3) a catalytically effective amount of one or more metals selected from rhodium (Rh), cobalt (Co), platinum (Pt), ruthenium (Ru), iron (Fe), thulium (Tm), cerium (Ce), yttrium (Y), neodymium (Nd), aluminum (Al), praesodymium (Pr) holmium (Ho), copper (Cu), samarium (Sm), europium (Eu), hafnium (Hf), manganese (Mn), vanadium (V), chromium (Cr), gold (Au), terbium (Tb), lutetium (Lu), nickel (Ni), scandium (Sc) and niobium (Nb) deposited on a support, i.e., carrier.

In another aspect, the present invention relates to an efficient aqueous process for the manufacture of high purity tetrahydrofuran comprising continuous hydrogenation of a hydrogenatable tetrahydrofuran precursor in the presence of a suitable hydrogenation catalyst in a back mixed

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reactor and maintaining the concentration of the acid
in the reaction mixture within a predetermined range.

DESCRIPTION OF RELATED ART

5   Numerous catalysts are disclosed in the art
as being useful for preparing tetrahydrofuran ("THF")
and 1,4-butanediol ("BDO") by the hydrogenation of
suitable THF precursors such as maleic acid, maleic
anhydride, fumaric acid, succinic acid, malic acid,
10   dimethyl succinate and gamma-butyrolactone. Many of
these catalysts incorporate the metals palladium and
rhenium on a suitable support. For example, U.S.
Patent 4,609,636 describes the use of a catalyst
composite comprising palladium and rhenium on a carbon
15   support for making THF, BDO or mixtures thereof from a
variety of hydrogenatable precursors. U.S. Patent
4,973,717 discloses the batchwise or continuous
production of an alcohol and/or ether from a
carboxylic acid ester using, for example, a palladium
20   based catalyst and further discloses the important
effect of a metal capable alloying with palladium.
The use of these alloyed catalysts for the direct,
selective production of THF/BDO from precursors
containing one or more carboxylic acid groups is not
25   disclosed in U.S. Patent 4,973,717.
         Methods are known in the art for the
selective production of THF by the catalytic reduction
of hydrogenatable precursors. For example, U.S.
Patent 4,609,636 teaches that the relative ratio of
30   THF to BDO can be increased by increasing one or more
variables selected from operating temperature, contact
time, and hydrogen spacetime. It is also known from
numerous references, such as U.S. Patent 3,726,905,
that the dehydration of BDO to give THF is catalyzed
35   by acid and that increasing the acid concentration

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results in an increase in the relative ratio of THF to
BDO. However, it is also known that rhenium
containing hydrogenation catalysts are inhibited by
acids in the presence of water. Bulletin of The Japan
5   Petroleum Institute, Volume 12, pages 89 to 96 (1970)
describes a "kinetic study of the hydrogenation of
maleic anhydride and intermediates using nickel-
rhenium catalyst on kieselguhr" and reports that
"water and succinic acid may be considered as the
10   chief inhibitor components" of the step involving the
reduction of the intermediate succinic anhydride to
gamma-butyrolactone. The authors conclude that "in
order to make the THF production rate greater, it is
necessary to decrease the concentration of succinic
15   acid as much as possible".

        Other known catalysts and processes for the
production of THF from hydrogenatable precursors are
cited in the above mentioned teachings, and are useful
for their intended purposes, however, all are subject
20   to improvement.

        One important area subject to improvement is
catalyst performance, i.e., selectivity, space time
yield and activity. Selectivity is defined herein to
refer to a measure of the percentage of the exit
25   stream composed of THF/BDO/gammabutyrolactone ("GBL")
in a plug flow reactor or a back-mixed reactor. Space
time yield (STY) is defined herein to refer to the
amount of grams of THF/kilogram catalyst/hour.
Activity is defined herein to refer to the percent
30   acid converted at a given hold up time in a plug-flow
reactor. Another important area subject to
improvement is the preferential production of THF
using catalysts that give both high selectivity and
high space time yield. Such improvements are of great
35   commercial significance since they allow for the more

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economical production of THF which is an item of
commerce with a plurality of uses. For example,
tetrahydrofuran is a useful solvent for high polymers,
such as polyvinyl chloride and as a monomer in
5   polyether polyols.
           It has been discovered in the present
invention that the process for making tetrahydrofuran
in a back-mixed or plug-flow reactor using a highly
active polymetallic palladium-rhenium catalytic
10   composite including one or more metals selected from
rhodium, cobalt, platinum, ruthenium, iron, thulium,
cerium, yttrium, neodymium, aluminum, praesodymium,
holmium, copper, samarium, europium, hafnium,
manganese, vanadium, chromium, gold, terbium,
15   lutetium, nickel, scandium and niobium produces high
space time yields of THF while maintaining high
selectivity in a back mixed reactor or produces a high
acid conversion in a plug flow reactor.
           It has also been discovered in the present
20   invention that, in the continuous manufacture and
removal by vapor take off of THF under back-mixed
conditions with a highly active catalyst in an aqueous
medium, maintaining the concentration of carboxylic
acids within a predetermined range results in high
25   selectivity to THF with very little over reduction and
surprisingly little loss in catalyst activity.

SUMMARY OF THE INVENTION
           According to the present invention a
30   hydrogenatable precursor such as maleic acid, maleic
anhydride, fumaric acid, succinic acid, succinic
anhydride, malic acid, or mixtures thereof, i.e.,
these precursors can be described as dicarboxylic
acids, or anhydrides, or mixtures of said acids and/or
35   anhydrides, is reacted with hydrogen in a back-mixed

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reactor or in a plug flow reactor at a temperature of
about 150°C to 300°C at a pressure of about 1000 to
3000 psig in the presence of a novel tri- or
polymetallic catalytic composite comprising a

5   combination of a catalytically effective amount of
palladium, rhenium and one or more metals (M), i.e., a
metal component selected from rhodium, cobalt,
platinum, ruthenium, iron, thulium, cerium, yttrium,
neodymium, aluminum, praesodymium, holmium, copper,

10   samarium, europium, hafnium, manganese, vanadium,
chromium, gold, terbium, lutetium, nickel, scandium
and niobium deposited on a support such as an
activated, porous carbon carrier with a surface area
in excess of about 650 m^2/g or a refractory oxide

15   carrier, e.g., alumina, zirconia, titania, hafnium
oxide, silica or barium carbonate and the like, to
produce high space time yields of THF while
maintaining high selectivity in a back mixed reactor
or to produce high acid conversion in a plug flow

20   reactor. The polymetallic catalytic composites of
this invention consist by total weight of: (1) from
about 0.1 to 10 weight percent of a palladium
component; (2) from about 1 to 20 weight percent of a
rhenium component; and, (3) from about 0.01 to 1.0

25   weight percent of the metal component with the
remaining weight comprising either an activated,
porous carbon carrier or a refractory oxide carrier.

     In another aspect of this invention, a
hydrogenatable precursor is reacted on a continuous

30   basis in an aqueous medium with hydrogen in a
back-mixed reactor at a temperature of about 150°C to
300°C at a pressure of about 1000 to 3000 psig in the
presence of a suitable hydrogenation catalyst with
continuous THF removal by vapor take off, and the

35

concentration of acid in the reaction mixture is
maintained within a predetermined range.

DETAILED DESCRIPTION OF THE INVENTION
Catalyst and Preparation

One aspect of the invention relates to a
novel tri- or polymetallic catalytic composite
consisting essentially of a combination of: (1) a
catalytically effective amount of palladium (Pd); (2)
a catalytically effective amount of rhenium (Re); and,
(3) a catalytically effective amount of one or more
metals (M), i.e., a metal component selected from
rhodium (Rh), cobalt (Co), platinum (Pt), ruthenium
(Ru), iron (Fe), thulium (Tm), cerium (Ce), yttrium
(Y), neodymium (Nd), aluminum (Al), praesodymium (Pr),
holmium (Ho), copper (Cu), samarium (Sm), europium
(Eu), hafnium (Hf), manganese (Mn), vanadium (V),
chromium (Cr), gold (Au), terbium (Tb), lutetium (Lu),
nickel (Ni), scandium (Sc) and niobium (Nb) deposited
on a support. The tri- or polymetallic catalytic
composite consists essentially of about 0.1 to 10
weight percent of palladium, about 1 to 20 weight
percent of rhenium and about 0.01 to 1.0 weight
percent of the metal or metals M by total weight.
It is the addition of the metal or metals M that
unexpectedly improves catalytic performance. Suitable
supports include activated, porous carbons and
refractory oxide carriers, e.g., alumina, zirconia,
titania, hafnium oxide, silica or barium carbonate and
the like. The preferred carrier is an activated,
porous carbon carrier. Suitable carbon supports have
a surface area in excess of about 650 m^2/g (measured
using standard N_2 BET techniques), typically in excess
of about 1000 m^2/g, preferably in excess of about 1500
m^2/g· The catalyst carbon support is fine powder

particles for use in a slurry reactor or larger
support granules for use in a fixed bed reactor.

The tri- or polymetallic catalytic composite
of this invention can be prepared in any one of a

5   number of different methods known in the art. How-
ever, a preferred step in the method for preparing
said catalyst involves sequential deposition of the
palladium component and the rhenium component as
described in greater detail in U.S. Patent 4,609,636,

10   the teachings of which are incorporated herein by
reference. For example, a method for preparing said
catalyst includes, in sequence, the steps of:

        (a) impregnating a carbon support with a
        solution containing sources of the metal M

15   and palladium and removing the solvent;
        (b) drying the metal M and palladium
        impregnated carbon at a temperature in the
        range of from 100°C to 500°C, under reducing
        conditions for about 0.5 to 24 hours;

20   (c) applying to the metal M and palladium
        impregnated carbon a source of rhenium in
        solution and removing the solvent to form
        said catalyst; and
        (d) drying the metal M/palladium/rhenium

25   impregnated carbon at a temperature in the
        range of from 100°C to 500°C, under reducing
        conditions for about 0.5 to 24 hours.

It will be appreciated by those skilled in
the art that variants of this method in which the

30   source of metal (M) is applied to the support and
reduced prior to the addition of the palladium, after
the addition of the palladium, after the addition of
the rhenium or simultaneously with the rhenium can
also be be eficially employed to prepare the catalysts

35   of this invention. This is illustrated by Examples

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65-67 which show that a catalyst prepared by an
alternate sequence of metal deposition (Rh deposited
and reduced before Pd, Example 30) gives similar
performance properties.

The solution containing the palladium
compound is typically an aqueous medium containing an
amount of palladium compound to yield a catalyst
product with the requisite amount of palladium. The
palladium compound is typically $PdCl_2$ and can also be,
but is not limited to, a palladium compound such as
$PdBr_2$, $Pd(NO_3)_2$, $Pd(C_2H_3O_2)_2$ (wherein $C_2H_3O_2$ denotes
acetate), $Pd(C_5H_7O_2)_2$ (wherein $C_5H_7O_2$ denotes
acetylacetonate), and coordination compounds such as
$(NH_3)_4PdCl_2$ or $(NH_4)_2PdCl_6$. The solution containing
the rhenium compound is typically an aqueous one
containing an amount of rhenium compound to yield a
catalyst product with the requisite amount of rhenium.
The rhenium compound is typically Re_2O_7 but can be
perrhenic acid or a perrhenate of ammonium or of an
alkali metal, K_2ReCl_6, $(C_2H_3O_2)_2ReCl$, or $(NH_4)_2Re_2Cl_8$,
etc. The solution containing the metal compounds M
are typically aqueous and contain an amount of metal
sufficient to yield a catalyst product with the
requisite metal loading. By way of example, when the
metal is rhodium, the rhodium compound is typically
$RhCl_3*xH_2O$ but can also be a rhodium compound such as
$RhBr_3*xH_2O$, $Rh_2(C_2H_3O_2)_4$, $Rh_6(CO)_{16}$, $Rh_4(CO)_{12}$,
$(Rh(CO)_2Cl)_2$, $Rh(C_5H_7O_2)_3$ or $Rh(NO_3)_3*2H_2O$, $Rh_2(SO_4)_3$,
as well as salts thereof exemplified by Na_3RhCl_6, and
$(C_4H_9)_4NRh(CO)_2Cl_2$, and coordination compounds where
Rh is ligated, for example by amines, halides,
carboxylates, carbon monoxide, etc., exemplified by
$Rh(NH_3)_6Cl_3$. When the metal is iron, the iron
compound is typically $FeCl_3*6H_2O$ but can also be an
iron compound such as $FeCl_2*xH_2O$, $FeBr_2$,

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$Fe(NO_3)_3*9H_2O$, $Fe(SO_4)*7H_2O$, $Fe_2(SO_4)_3$, $Fe(C_5H_7O_2)_3$, $(C_5H_5)_2Fe$ (wherein C_5H_5 denotes cyclopentadienyl), $Fe(CO)_5$, $Fe_2(CO)_9$, as well as salts and coordination compounds thereof. When the metal is cobalt, the cobalt compound is typically $CoCl_2*6H_2O$ but can also be a cobalt compound such as $CoBr_2*xH_2O$, $Co(OH)_2$, $Co(NO_3)_2*6H_2O$, $CoSO_4*7H_2O$, $Co(C_2H_3O_2)_2$, Co_3O_4, $Co(C_5H_7O_2)_2$, $Co(C_5H_7O_2)_3$, $Co_2(CO)_8$, coordination compounds such as $Co(NH_3)_6Cl_3$, and salts such as $Co(ClO_4)_2$. When the metal is platinum, the platinum compound is typically $H_2PtCl_6*6H_2O$, but can also be a platinum compound such as $PtCl_2$, Na_2PtCl_4, $PtCl_4$, $PtBr_2$, $PtBr_4$, H_2PtBr_6, $H_2Pt(OH)_6$, $Pt(C_5H_7O_2)_2$, coordination compounds such as $(NH_4)_2PtCl_4$, $(C_2H_8N_2)_3PtCl_4$, or $(NH_3)_4Pt(NO_3)_2$, and organometallic precursors such as $(n-C_4H_9)_4NPtBr_3(CO)$. When the metal is ruthenium, the ruthenium compound is typically $RuCl_3*3H_2O$, but can also be a ruthenium compound such as $RuBr_3*xH_2O$, $RuNO(NO_3)_3$, RuO_2*xH_2O, $Ru(C_5H_7O_2)_3$, $Ru_2(C_2H_3O_2)_4Cl$, coordination compounds such as $Ru(NH_3)_5Cl_3$ and $(NH_4)_2Ru(H_2O)Cl_5$, $(NH_4)_2RuCl_6$, and organometallic compounds such as $Ru_3(CO)_{12}$. When the metal is thulium, the thulium compound is typically $TmCl_3*7H_2O$, but can also be a thulium compound such as $TmBr_3*xH_2O$, TmF_3, TmI_3, Tm_2O_3, $Tm(C_2H_3O_2)_3*xH_2O$, $Tm(C_5H_7O_2)_3$, $Tm_2(CO_3)_3*xH_2O$, and $Tm(NO_3)_3*5H_2O$. When the metal is cerium, the cerium compound is typically $CeCl_3*xH_2O$, but can also be a cerium compound such as $CeBr_3*6H_2O$, CeF_3, CeI_3, $Ce_2(C_2H_3O_2)_3*3H_2O$, $Ce_2(CO_3)_3*5H_2O$, $Ce(NO_3)_3*6H_2O$, $Ce(C_5H_7O_2)_3$, as well as salts such as $(NH_4)2Ce(NO_3)_6$. When the metal is yttrium, the yttrium compound is typically YCl_3*6H_2O, but can also be a yttrium compound such as YBr_3*xH_2O, YF_3, Y_2O_3, $Y(C_2H_3O_2)_3*4H_2O$, $Y(C_5H_7O_2)_3$, $Y(C_3H_7O)_3$, $(C_5H_5)_3Y$,

$Y_2(CO_3)_3*3H_2O$, and $Y(NO_3)_3*6H_2O$. When the metal is neodymium, the neodymium compound is typically $NdCl_3*6H_2O$, but can also be a neodymium compound such as $NdBr_3*xH_2O$, NdF_3, NdI_3, Nd_2O_3, $Nd(C_2H_3O_2)_3*H_2O$, $Nd(C_5H_7O_2)_3$, $Nd(NO_3)_3*6H_2O$ and $Nd_2(CO_3)_3*xH_2O$. When the metal is aluminum, the aluminum compound is typically $AlCl_3*6H_2O$, but can also be an aluminum compound such as $AlCl_3$, $AlBr_3$ and hydrates, AlF_3 and hydrates, AlI_3, $Al(OH)_3$, $Al(C_3H_7O)_3$ (wherein C_3H_7 is isopropoxide), $Al(C_5H_7O_2)_3$, and $Al(NO_3)_3*9H_2O$. When the metal is praesodymium, the praesodymium compound is typically $PrCl_3*7H_2O$, but can also be a praesodymium compound such as $PrBr_3$ and hydrates, PrF_3, PrI_3, Pr_6O_{11}, $Pr(C_2H_3O_2)_3*3H_2O$, $Pr(C_5H_7O_2)_3$, $Pr_2(CO_3)_3*8H_2O$ and $Pr(NO_3)_3*6H_2O$. If the metal is holmium, the holmium compound is typically $HoCl_3*6H_2O$, but can also be a holmium compound such as $HoBr_3$ and hydrates, HoF_3, HoI_3, Ho_2O_3, $Ho(C_5H_7O_2)_3$, $Ho(C_2H_3O_2)_3*xH_2O$, $Ho_2(CO_3)_3*xH_2O$ and $Ho(NO_3)_3*5H_2O$. The M precursor can be any M compound with properties suitable for the catalyst preparation, e.g., soluble in the solvent of choice. Suitable compounds include oxides, carbonates, alkoxides, -diketonates, halides, nitrates, sulfates, hydroxides, carboxylates, carbonyls, coordination compounds and combinations of the above as well as solvates and salts thereof. A preferred M compound is of the general formula MCl_x*xH_2O.

The preparation of the catalyst composite may be carried out in the presence of Group IA or IIA metals, which may be present in the carbon as obtained or may be added. For example, t e beneficial effect of the addition of potassium is s own in Example 70. It is believed that addition of po ssium to the slurry catalyst of the present inventi n can be

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beneficially employed in a slurry reactor. The fixed
bed catalyst support carbon contains potassium as
obtained.

5   Catalytic Process for Preparing THF
                    Another aspect of the present invention
          involves the catalytic process for preparing THF,
          employing the tri- or polymetallic catalytic composite
          described above, in a back-mixed reactor to achieve a
10   high space time yield, e.g., in excess of about 280 g
          THF/kg catalyst/hr in a back-mixed reactor while
          maintaining high selectivity, e.g., up to about 90%.
          Alternatively, the process can be carried out in a
          plug flow reactor with a catalyst of the present
15   invention exhibiting high activity, e.g., in excess of
          58% acid conversion of a 5% by weight maleic acid feed
          at 250°C, 2000 psig total pressure and a contact time
          of 0.016 hour. More preferred composites employed in
          the process are those wherein the r tal component is
20   selected from rhodium, cobalt, platinum, ruthenium,
          iron, thulium, cerium, yttrium, neodymium, aluminum,
          praesodymium and holmium.
                    The hydrogenatable precursors, i.e.,
          starting reactants useful for carrying out the
25   invention are, for example, maleic acid, maleic
          anhydride, fumaric acid, succinic acid, succinic
          anhydride, malic acid, or mixtures thereof. These
          precursors can be described as dicarboxylic acids, or
          anhydrides, or mixtures of said acids and/or
30   anhydrides. Preferred hydrogenatable precursors
          include maleic acid and malic anhydride For
          example, using these precursors in aqueou solution,
          the process is believed to p ceed in a st pwise
          manner with maleic acid (MAC) rst being r uced to
35   succinic acid (SAC) which is further reduced to

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reduced directly to THF, but is also reduced to BDO
which is finally dehydrated to THF. By products
include alcohols (1-propanol (PrOH) and 1-butanol
(BuOH)) and alkanes (primarily butane, methane). It
5   will be appreciated by those skilled in the art that
the process of this invention is equally applicable to
the production of 3-methyltetrahydrofuran. Suitable
hydrogentable precursors to 3-methylTHF include, but
are not limited to, itaconic acid, itaconic anhydride,
10   citraconic acid, citraconic anhydride, mesaconic acid,
citric acid and aconitic acid. Itaconic acid is a
preferred precursor due to cost and ease of reduction.
It is further recognized that analogous precursors to
other substituted THFs, such as 3-ethylTHF and
15   3-propylTHF can be beneficially employed in the
process of this invention.
        Production of THF includes the hydrogenation
of the hydrogentable precursor in an aqueous or
organic solvent medium, i.e., the precursor solution
20   is reacted with hydrogen in a back-mixed reactor or in
a plug flow reactor. A preferred solvent for the
process of this invention is water. The hydrogenation
conditions include a reaction temperature in the range
of about 150°C to 300°C, preferably about 250°C and a
25   hydrogen pressure of about 1000 to 3000 psig,
preferably about 2000 psig, a hydrogen spacetime of
about 1 to 14 minutes and a liquid contact time of
about 0.5 to 7 hours in the presence of the tri- or
polymetallic catalytic composite described above. The
30   hydrogenation of this invention can be run using
conventional apparatus and techniques in a back-mixed
or plug flc reactor. Hydrogen is fed continuousl ,
generally .n considerable stoichiometric excess.
Unreacted hydrogen can be returned to the reactor as ¬
35   recycled stream. The precursor solution, e.g., maleic

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acid-water solution, is fed continuously at
concentrations ranging from dilute solutions to near
the maximum solubility level; typically the
concentration is between about 30 to 40 weight
5   percent. The catalyst carbon support is fine powder
particles for use in a slurry reactor or larger
support granules for use in a fixed bed reactor. The
amount of catalyst required will vary widely and is
dependent upon a number of factors such as reactor
10   size and design, contact time and the like.
        One method for carrying out the invention is
in a plug flow reactor as described in greater detail
in the examples. The selectivity was a measure of
what percent of the exit stream is composed of THF,
15   BDO and GBL. The highly active catalysts of this
invention, when tested in a plug flow reactor,
typically exhibit higher activity, and comparable
selectivity, than a similarly prepared bimetallic
Pd,Re/C catalyst. The loss of selectivity observed in
20   some cases may be caused by over hydrogenation. If
the catalyst is highly active but unselective at a
certain temperature, decreasing its activity by
lowering the temperature increases selectivity.
Operating at lower temperatures can be an advantage in
25   itself.
        A preferred method of preparing THF is in a
back-mixed reactor such as, for example, a continuous
slurry reactor. It has been discovered in the present
invention that the higher activity of the tri- or
30   polymetallic catalytic composite described above can
be most effectively utilized to give high STY and
selectivity to THF in this type of reactor.   hile
this reactor configuration results in a high
concentration of aqueous carboxylic acids in the
35   reactor, it has surprisingly been found that highly

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active palladium/rhenium-on-carbon catalysts, such as
those described herein and in U. S. Patent 4,609,636,
still perform well in a reaction mixture containing
high concentration of acid. One major advantage of
5   the back-mixed reactor, which is particularly
well-suited for producing THF from maleic acid, is
vapor take off of THF, i.e., the THF can be purged
from the reactor shortly after being formed, thus
minimizing "over-hydrogenation", i.e., further
10   reduction of the desired THF product, to form less
desirable alcohols and alkanes. A second advantage of
the back-mixed reactor is that acid in the feed is
distributed throughout the reaction mass, and is thus
available to catalyze the last step in the maleic acid
15   to THF sequence, i.e., the ring closing of BDO to THF.
This is of critical importance since it has been found
that the BDO is also subject to over hydrogenation and
a rapid conversion of BDO to THF serves to minimize
yield losses due to over reduction of the BDO. It
20   will be appreciated by those skilled in the art that
these two features of a back-mixed reactor contribute
to the ability to use the catalyst of higher activity
without loss in selectivity. Alternatively, a fixed
bed reactor with adequate recycle such that it
25   approximates a back-mixed reactor can be used to carry
out the invention.

Tetrahydrofuran and 1,4-butanediol are the
products produced by the process of this invention in
a plug flow reactor or in a back-mixed reactor. The
30   catalysts and processes of this invention are
particularly well suited for the manufacture of THF.
Another aspect of the invention is the production of
THF in an essentially back-mixed reactor using a
continuous process which provides definite advantages
35   for separation and recovery of THF, for example: (1)

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THF and over reduced by products are volatile and can
be distilled out of a back mixed reactor as they are
formed and, if necessary, the THF further purified
using conventional procedures; (2) the maleic acid
5   starting material and the intermediates (up to and
including BDO) are less volatile and tend to remain
behind in the reactor; and (3) small amounts of THF
precursors or intermediates, such as GBL, which are
swept out with the THF can be separated and recycled
10   to the reactor. In the continuous hydrogenation
process of this invention, the BDO and THF are
initially produced and the relative amounts obtained
are dependent upon the nature of the catalyst employed
as well as other factors such as those described in
15   U.S. patent 4,609,636. The conversion of BDO produced
to THF does not require further hydrogenation, but
only an acid-catalyzed ring closure. This conversion
is readily achieved in a back mixed reactor where the
concentration of the carboxylic acids in the reaction
20   mixture is maintained within a predetermined range,
e.g., between about 1% and 10% by weight (calculated
as succinic acid) of the reaction mixture. Preferably
the concentration of carboxylic acids in the reaction
mixture is maintained in excess of about 3% by weight
25   of the reaction mixture. Better STY and selectivity
is obtained above 3% by weight while fewer operational
problems associated with acid solidification in
process equipment are encountered below about 10%,
typically about 8% by weight. This continuous process
30   is particularly well suited for use with certain
highly active hydrogenation catalysts which comprise a
bi-, tri-, or polymetallic catalytic composite of fine
metallic particles on an activated porous carbon
support. For example, catalysts for use in this
35   continuous process are comprised of, by total weight,

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from about 0.1 to 10 weight percent of palladium,
about 1 to 20 weight percent of rhenium and optionally
from about 0.01 to 1.0 weight percent of a component
containing one or more of the metals selected from
5   rhodium, cobalt, platinum, ruthenium, iron, thulium,
cerium, yttrium, neodymium, aluminum, praesodymium,
holmium, copper, samarium, europium, hafnium,
manganese, vanadium, chromium, gold, terbium,
lutetium, nickel, scandium and niobium on a carbon
10   support having a surface area in excess of about 1000
m^2/g. A preferred hydrogenatable precursor for use in
this continuous process is aqueous maleic acid. In
the continuous process of the present invention, the
required acid is provided by maleic, succinic, and to
15   a lesser extent, other acids distributed throughout
the reaction mixture in the back-mixed reactor. Thus,
by controlling acid levels according to the process of
this invention, high selectivity to THF can be
obtained regardless of the relative amounts of BDO and
20   THF initially produced with very little over reduction
and surprisingly little loss in catalyst activity. It
will be appreciated by those skilled in the art that
the continuous process of this invention is equally
applicable to the production of 3-methyltetrahydro-
25   furan. Suitable hydrogentable precursors to 3-methyl-
THF include, but are not limited to, itaconic acid,
itaconic anhydride, citraconic acid, citraconic
anhydride, mesaconic acid, citric acid and aconitic
acid. Itaconic acid is a preferred precursor due to
30   cost and ease of reduction. It is further recognized
that analogous precursors to other substituted THFs,
such as 3-ethylTHF and 3-propylTHF can be beneficially
employed in the continuous process of this invention.

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The following examples serve to illustrate
the invention, but are not intended to limit the scope
of the invention.

5   EXAMPLE 1
        An example of a preparation of a catalyst
suitable for use in a slurry reactor is presented.
Note that the items in parentheses refer to the
parameter headings in Table 1. The remaining
10   preparations of slurry catalysts, i.e., Examples 2-4
were done in the same way; the parameters used in the
preparation of Examples 2-4 are listed in Table 1.
        This example describes the preparation of a
Rh+Pd,Re/C trimetallic catalytic composite of the
15   present invention, suitable for use in a slurry
reactor (type). The notation M+Pd,Re/C is meant to
imply that M and Pd were codeposited and reduced
followed by Re deposition and reduction.
        0.24 g RhCl$_3$*H$_2$O (M precursor) containing
20   0.10 g Rh(Wt M) was dissolved in 115 ml H$_2$O. 3.30 ml
(vol 1 = 115+3.3) PdCl$_2$-HCl stock solution containing
0.5 g Pd (Wt Pd) was added. The solution was added to
50g (wt Cl) Darco KBB© carbon, commercially available,
and the resulting slurry was stirred occasionally over
25   a 3 hour period at room temperature. The slurry was
dried overnight at 115°C. The Rh,Pd/C powder was
recovered and then reduced at 300°C in flowing H$_2$-He
(1:1) for eight hours. The reduced powder was cooled
to 50°C, purged with He, cooled to room temperature in
30   flowing He, and then passivated 30 minutes in flowing
1% O2 in N$_2$. A solution was prepared by adding 13.1
ml of a Re$_2$O$_7$-H$_2$O stock solution containing 1.03 g Re
(wt Re) to 77ml (vol 2=13.1+77) H$_2$O. This solution
was added to 36.4 g (wt C$_2$) of reduced Rh,Pd/C and
35   stirred occasionally for 3 hours at room temperature.

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The Rh,Pd,Re/C sample was dried, reduced and
passivated as above. Nominal loadings are 0.2% Rh(%
M), 1.0% Pd(% Pd), and 2.8% Re(% Re). Nominal loading
is defined as 100*wt metal/wt support
5   composite(support + any metals previously deposited).

Example 5

        This example describes the preparation of a
trimetallic Rh+Pd,Re/C catalytic composite of the
10   present invention suitable for use in the fixed bed
reactor. Note that the items in parentheses refer to
the parameter headings in Table 1. The preparations
of fixed bed catalysts of Examples 5-12 were done in
the same way; the parameters used in the preparation
15   of Examples 5-12 are listed in Table 1.
        0.064 g $RhCl_3$*xH_2O(M precursor) containing
0.027 g Rh(Wt M) was added to 0.65 ml $PdCl_2$-HCl stock
solution containing 0.099 g Pd(Wt Pd). 18ml H_2O(vol
1= 0.65+18) was added and mixed well. The solution
20   was added to 10g(Wt Cl) Calgon PCB® 12x30 carbon
(commercially available), which had been calcined at
400°C for two hours in air and the resulting slurry
was stirred occasionally over a 3 hour period at room
temperature. The slurry was dried overnight at 115°C.
25   The Rh,Pd/C powder was recovered and then reduced at
300°C in flowing H_2-He (1:1) for eight hours. The
reduced powder was cooled to 50°C, purged with He,
cooled to room temperature in flowing He, and then
passivated 30 minutes in flowing 1% O_2 in N_2. A
30   solution was prepared by adding 3.76 ml of a Re_2O_7-H_2O
stock solution containing 0.29 g Re(Wt Re) to 10 ml
H_2O(vol 2=3.76+10). This solution was added to 8.0 g
of reduced Rh,Pd/C(Wt C_2) and stirred occasionally for h
3 hours at room temperature. The Rh+Pd,Re/C sample
35   was dried, reduced and passivated as above. Nominal

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loadings are 0.3% Rh(% M), 1.0% Pd(% Pd), and 3.6%
Re(% Re).

The catalysts of Examples 13-29 were
prepared similarly, but a slightly different reduction
5   protocol was used. The preparation of Example 13 is
described in detail to indicate these slight
differences. The preparation parameters for Examples
13-29 are listed in Table 1.

10   Example 13
0.22 g $TmCl_3*_7H_2O$(M precursor) containing
0.093g Tm(Wt M) was added to a solution of 1.00 ml
$PdCl_2$-HCl stock solution containing 0.147 g Pd(Wt Pd)
in 29ml H_2O (vol 1= 1.00+29) and mixed well. 15g(Wt
15   Cl) Calgon PCB® 12x30 carbon (commercially available)
which had been calcined at 400°C in air for 2 hours,
was added to the solution and the resulting slurry was
stirred occasionally over a 3 hour period at room
temperature. The slurry was dried overnight at 115°C.
20   The Tm,Pd/C powder was recovered and then reduced at
300°C in flowing H_2-He (3:97) for 5.8 hours. The
reduced powder was purged with He at 300°C for 0.5
hour, cooled to room temperature overnight (>5 hours)
in flowing He. A solution was prepared by adding 6.5
25   ml of a Re_2O_7-H_2O stock solution containing 0.52 g
Re(Wt Re) to 19.5 ml H_2O (vol 2=6.5+19.5). To this
solution was added 13.0 g of reduced Tm,Pd/C(Wt C_2)
and stirred occasionally for 3 hours at room
temperature. The Tm+Pd,Re/C sample was dried and
30   reduced as above. Nominal loadings are 0.6% Tm(% M),
1.98% Pd(% Pd), and 4.0% Re(% Re).

The Rh,Pd,Re/C catalyst of Example 30 was
prepared using a different sequence of metal
deposition from previous examples. Rh was deposited
35   on the carbon support and reduced. Pd was next

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deposited and reduced, and then Re was deposited and
reduced.

                        Example 30

5   0.094 g RhCl$_3$*xH$_2$O containing 0.040 g Rh was
added to 36ml H$_2$O and mixed well. To this solution
was added 20g of Calgon PCB® 12x30 carbon
(commercially available) which had been calcined at
400°C in air for 2 hours, and the resulting slurry was
10   stirred occasionally over a 3 hour period at room
temperature. The slurry was dried overnight at 115°C.
The Rh/C powder was recovered and then reduced at
300°C in flowing H$_2$-He (1:1) for eight hours. The
reduced powder was cooled to 50°C, purged with He,
15   cooled to room temperature in flowing He, and then
passivated 30 minutes in flowing 1% O$_2$ in N$_2$. A
solution was prepared by adding 1.12 ml of a PdCl$_2$-HCl
stock solution containing 0.17 g Pd to 30 ml H$_2$O. To
this solution was added 16.8 g of reduced Rh/C and
20   stirred occasionally for 3 hours at room temperature.
The Rh,Pd/C sample was dried, reduced and passivated
as above. A solution was prepared by adding 4.80 ml
of a Re$_2$O$_7$-H$_2$O stock solution containing 0.38 g Re to
15 ml H$_2$O. To this solution was added to 8.0 g of
25   reduced Rh,Pd/C and stirred occasionally for 3 hours
at room temperature. The Rh,Pd,Re/C sample was dried,
reduced and passivated as above. Nominal loadings are
0.2% Rh, 1.0% Pd, and 4.8% Re.

30   Comparative Example A
     Preparation of a Bimetallic Pd,Re/C Slurry Catalyst
              6.30 ml PdCl$_2$-HCl stock solution
containing 0.96 g Pd was added to 224 cc water. The
solution was added to 77g Darco KBB® carbon,
35   commercially available, and the resulting slurry was

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stirred occasionally over a 3 hour period at room
temperature. The slurry was dried overnight at 115°C.
The Pd/C powder was recovered and then reduced at
300°C in flowing H_2-He (1:1) for eight hours. The

5   reduced powder was cooled to 50°C, purged with He,
cooled to room temperature in flowing He, and then
passivated 30 minutes in flowing 1% O_2 in N_2. A
solution was prepared by adding 36.3 ml of a Re_2O_7-H_2O
stock solution containing 2.78g Re to 200ml H_2O. This

10   solution was added to 71.0g of reduced Pd/C and
stirred occasionally for 3 hours at room temperature.
The Pd,Re/C sample was dried, reduced and passivated
as above. Nominal loadings are 1.25% Pd and 3.9% Re.

15   Comparative Example B
             Preparation of a Bimetallic Pd,Re/C
                     Fixed Bed Catalyst
             6.80 ml $PdCl_2$-HCl stock solution containing
     1.01 g Pd was added to 172cc water and mixed well.
20   The solution was added to 100g Calgon PCB® 12x30
     carbon (commercially available) which had been
     calcined at 400°C in air for 2 hours and the resulting
     slurry was stirred occasionally over a 3 hour period
     at room temperature. The slurry was dried overnight
25   at 115°C. The Pd/C powder was recovered and then
     reduced at 300°C in flowing H_2-He (1:1) for eight
     hours. The reduced powder was cooled to 50°C, purged
     with He, cooled to room temperature in flowing He, and
     then passivated 30 minutes in flowing 1% O_2 in N_2. A
30   solution was prepared by adding 45.1 ml of a Re_2O7-H_2O
     stock solution containing 3.60 g Re(Wt Re) to 116 ml
     H_2O. This solutic was added to 90 g of reduced Pd/C
     and st rred occasic. ally for 3 hours at room
     temperature. The Pd,Re/C sample was dried, reduced

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and passivated as above. Nominal loadings are 1.0% Pd
and 4.0% Re.

Comparative Example C
Preparation of a Bimetallic Pd,Re/C
Slurry Catalyst Containing Potassium
1.91g KCl was dissolved in 230cc DI water
and mixed well. This mixture was added to 100g Darco
KBB® carbon, commercially available, and stirred
occasionally over a 3 hour period at room temperature.
The slurry was dried overnight at 115°C. 5.4 ml
PdCl$_2$-HCl stock solution containing 0.82 g Pd was
added to 192cc water and mixed well. The solution was
added to 85.1g K/C and the resulting slurry was
stirred occasionally over a 3 hour period at room
temperature. The slurry was dried overnight at 115°C.
The K,Pd/C powder was recovered and then reduced at
300°C in flowing H$_2$-He (1:1) for eight hours. The
reduced powder was cooled to 50°C, purged with He,
cooled to room temperature in flowing He, and then
passivated 30 minutes in flowing 1% O$_2$ in N$_2$. A
solution was prepared by adding 36.2 ml of a Re$_2$O$_7$-H$_2$O
stock solution containing 2.84g Re to 200ml H$_2$O. This
solution was added to 70.7g of reduced K,Pd/C and
stirred occasionally for 3 hours at room temperature.
The K,Pd,Re/C sample was dried, reduced and passivated
as above. Nominal loadings are 1.0%K, .96% Pd and
4.0% Re.

Catalyst Performance in a Back-Mixed Reactor
The catalyst fo. a back-mixed reactor was
tested by charging 7-1½ g (ry basis) of slurry
catalyst in 150 ml water to ₁ 300 ml Hastaloy C
autoclave, equipped with an a itator, a thermocouple,
feed lines for hydrogen and male'c acid, and an exit

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line through which the product was swept out with the
excess hydrogen and water. The catalyst was activated
by heating at 250°C under a 1000 ml/min hydrogen flow
at 2000 psig for one hour. The maleic acid was fed as
5   a 40% by weight aqeous solution at feed rates ranging
from 18 to 36 ml/min, and the reactor was maintained
at 2000 psig and 250°C. The volatile products and
water were swept out of the reactor at a rate
controlled by the hydrogen feed rate. The hydrogen
10   feed rate was adjusted so that the amount of water
carried out with the exiting hydrogen gas balances the
amount of water added with the maleic acid feed and
the amount produced by the reaction; the reactor level
was maintained at 100-200cc. Note that in all cases a
15   very large excess of hydrogen was fed, compared to the
amount consumed by the reaction; thus, the hydrogen
feed rate does not affect catalyst performance.

          Several different feed rates of maleic acid
were used in a catalyst test. Typically, the feed
20   rate was increased from run to run until optimum
performance was achieved. The reproducibility of this
optimum performance was then checked over two or more
runs at the same conditions.

          A catalyst test was made up of several runs.
25   Typically, each run lasts 8-12 hours, with the reactor
in steady state operation for 6-10 hours. The product
composition data generated during steady state
operation was averaged to give the average production
rates(g/hr) of THF, BDO, GBL, PrOH, BuOH, and alkanes
30   (primarily butane and methane). The product
composition data were measured in the following way.
A portion of the volatilized product/water in the
exit gas stream is condensed and collected as "liquid
product". The volume of the liquid product collected
35   each hour was measured, and its composition analyzed

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using a calibrated gas chromatograph (GC) equipped
with a flame ionization detector. The remaining
uncondensed product(THF and alkanes) still in the exit
gas stream was analyzed by measuring the gas flow

5   rate, then analyzing the gas stream every two hours,
using procedures similar to the one used for liquid
analysis. The reactor contents are sampled every four
hours and analyzed by GC and titration. The GC
analysis was carried out using a Supelcowax 10

10   capillary column (30 m X 0.052 milliliter) which was
maintained at 75°C for 5 minutes after injection and
then heated at 10°C per minute to a final temperature
of 200°C. The acid level in the mixture was measured
by titration with sodium hydroxide and reported as %

15   by weight of succinic acid. The combination of these
three analyses permits calculation of the catalyst's
performance (STY and selectivity) and the mass balance
for each run.

20   THF STY = wt THF produced/hr
                             1 kg catalyst

Selectivity=(moles/hr of (THF(gas) + THF(liq) +
GBL(liq) + BDO(liq))) / (moles/hr of (THF(gas) +

25   THF(liq) + GBL(liq) + BDO(liq)+ PrOH(liq) + BuOH(liq)
+ alkane(gas)))

The maximum observed THF STY for the 1%, 4% Pd,Re/C
slurry catalyst of comparative example A was 280 g

30   THF/kg catalyst/hr. The trimetallic catalyst of this
invention gave a THF STY in excess of 280 ; THF/kg
catalyst/hr. The selectivity was a measure of what
percentage of the exit stream was made up of THF, BDO
and GBL. The addition of rhodium greatly impoved

35   STY, while maintaining high selectivity.

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The back-mixed run results are summarized in Table 2.

Another aspect of the invention is control of the acid concentration in the reaction mixture within the range of about 1% and 10% by weight (calculated as succinic acid) of the reaction mixture. The bimetallic catalyst composite of Comparative Example A was run in several days in the backmixed reactor to demonstarate the beneficial effects of acid control. The results, listed in Table A, show the beneficial effects on STY and selectivity, e.g., increasing the acid concentration from about 3% to about 10% benefits STY and selectivity.

Table A
CATALYST PERFORMANCE: BACKMIXED SLURRY REACTOR[1]

Catalyst	Prepar-ation	Acid Feed Rate[2]	Acid Conc.[3]	THF (STY)	Selectivity (THF+ GBL+BDO)
Pd,Re/C	Ex.A	18 cc/hr	3.1%	216	83
		25	4.5	276	91
		31	8.0	280	91
		30	9.9	282	93

1 Hydrogenation of 40% maleic acid at 250°C in excess flowing H_2, 2000 psig total pressure.
2 Feed rate of 40% maleic acid/water in cc/hr.
3 Concentration of acid in the reactor, reported as wt% succinic acid, measured by acid-base titration.

The beneficial effects of increasing the concentration of acid in the reactor on STY and selectivity are apparent. Although not listed here, lower acid fee rates result in even lower acid concentration, STY a. selectivity.

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Catalyst Performance in a Plug Flow Reactor

One method of preparing THF is liquid phase
hydrogenation using conventional apparatus and
techniques in a plug flow reactor as described in
5   greater detail in U.S. Patent 4,609,636, the teachings
of which are incorporated herein by reference.

The catalyst for a plug flow reactor was
tested by charging 3 g of catalyst to a 1/4 inch
diameter Hastaloy U-tube reactor which was immersed in
10   a heated sand bath for temperature control. The
catalyst was activated by heating for one hour at
250°C in a 100 ml/min hydrogen flow at 2000 psig.
Hydrogen and maleic acid were co-fed to one end of the
reactor, and the liquid/gas stream exited from the
15   reactor through a pressure let-down valve which was
set to control the pressure at the desired level. The
excess gas was disengaged from the liquid in a chilled
separator held at 90 psig pressure. In these
experiments, the maleic acid was fed as a 5% aqueous
20   solution at flow rates ranging from 6 to 300 ml/hr.
Hydrogen flow was maintained in large excess at 100
to 200 ml/min. The temperature was maintained at
250°C and pressure at 2000 psig.

Each catalyst was evaluated at four
25   different maleic acid feed rates to adequately map its
performance characteristics. The gas and liquid was
analyzed by GC as described above. Since neither
maleic nor succinic acid is detected on the GC, the
concentration of (maleic + succinic) acids in the
30   product was determined directly by acid-base titration
and reported as weight % succinic acid.

The fixed bed performance data are
summarized in Table 3. The percent of acid converted
at a given hold up time is a measure of catalyst
35   activity. The selectivity to (THF + BDO + GBL) is the

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maximum observed in a fitted plot of selectivity vs
contact time for the four different flow rates. The
THF STY(g THF/kg catalyst/hr) is the curve maximum
from a fitted plot of STY vs contact time for the four
5   different flow rates.

The catalyst of this invention exhibited
higher activity, and comparable selectivity, than the
bimetallic Pd,Re/C catalyst of comparative Example B.
The loss of selectivity observed in some cases was
10   caused by "over-hydrogenation", i.e. reaction that
goes beyond the desired THF product, to form alcohols
and alkanes. Although the catalyst was too active at
this temperature, resulting in over-hydrogenation,
decreasing its activity by lowering the temperature
15   increased selectivity, as shown in Table 4. Operating
at lower temperatures can be an advantage in itself.

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TABLE 1
CATALYST PREPARATION

Ex.	Catalyst	Type	M pre-cursor	Wt(g) M/Pd/Re	Wt(g) C1	Vol 1/ Vol 2 (cc)	Wt(g) C2	Loading M/Pd/Re (%)
1	Rh+Pd,Re/C	slurry	$RhCl_3*H_2O$	.10/.5/1.03	50	118/90	36.4	.2/1.0/2.8
2	Ru+Pd,Re/C	slurry	$RuCl_3*3H_2O$	.10/.5/1.03	50	118.3/ 143.2	48	.2/1.0/2.1
3	Co+Pd,Re/C	slurry	$CoCl_2*6H_2O$	.12/.6/1.74	65	212.3/ 155	59.2	.2/.9/2.9
4	Fe+Pd,Re/C	slurry	$FeCl_3*6H_2O$	.050/.50/50		154/59	21/6	.1/1.0/4.0
5	Rh+Pd,Re/C	fixed bed	$RhCl_3*H_2O$	.027/.099/.29	10	19/14	8.0	.3/1.0/3.6
6	Ru+Pd,Re/C	fixed bed	$RuCl_3*3H_2O$	.026/.099/.29	10	19/14	8.0	.3/1.0/3.6
7	Co+Pd,Re/C	fixed bed	$CoCl_2*6H_2O$	.015/.099/.30	10	19/14	8.4	.15/1.0/3.6
8	Fe+Pd,Re/C	fixed bed	$FeCl_2*6H_2O$	.013/.099/.35	10	22/19	8.4	.15/1.0/4.2
9	Ni+Pd,Re/C	fixed bed	$NiCl_2*6H_2O$	.015/.099/.37	10	22/20	9.4	.15/.99/4.0
10	Au+Pd,Re/C	fixed bed	$AuCl_3$	.25/.505/1.92	50	90/87	48	.51/1.0/4.0
11	Pt+Pd,Re/C	fixed bed	$H_2PtCl_6*6H_2O$	0.015/.099/.36	10	19/15	8.9	.15/1.0/4.0
12	Mn+Pd,Re/C	fixed bed	$MnCl_2*4H_2O$	.031/.145/.52	15	30/26	13	.20/1.0/4.0
13	Tm+Pd,Re/C	fixed bed	$TmCl_3*7H_2O$	.093/.147/.52	15	30/26	13	.60/.98/4.0
14	Ce+Pd,Re/C	fixed bed	$CeCl_3*7H_2O$	.030/.154/.52	15	29/26	13	.20/1.0/4.0
15	Y+Pd,Re/C	fixed bed	YCl_3*6H_2O	.047/.154/.52	15	29/26	13	.31/1.0/4.0
16	Nd+Pd,Re/C	fixed bed	$NdCl_3*6H_2O$	.076/.147/.52	15	30/26	13	.51/.98/4.0
17	Al+Pd,Re/C	fixed bed	$AlCl_3*6H_2O$	.030/.154/.52	15	30/27	13	.20/1.0/4.0
18	Pr+Pd,Re/C	fixed bed	$PrCl_3*7H_2O$	.076/.154/.52	15	29/26	13	.51/1.0/4.0
19	Ho+Pd,Re/C	fixed bed	$HoCl_3*6H_2O$	.083/.147/.52	15	30/26	13	.55/9.8/4.0
20	Cu+Pd,Re/C	fixed bed	$CuCl_2*2H_2O$	.030/.154/.52	15	30/26	13	.20/1.0/4.0
21	Sm+Pd,Re/C	fixed bed	$SmCl_2*6H_2O$	.082/.147/.52	15	29/26	13	.55/1.0/4.0
22	Eu+Pd,Re/C	fixed bed	$EuCl_3$	.082/.147/.51	15	30/25	12.8	.55/.98/4.0
23	Hf+Pd,Re/C	fixed bed	$HfOCl_2$	.096/.147/.51	15	29/25	12.8	.64/.98/4.0
24	V+Pd,Re/C	fixed bed	VCl_3	.026/.147/.52	15	30/26	13	.18/1.0/4.0
25	Cr+Pd,Re/C	fixed bed	$CrCl_3*6H_2O$	.028/.151/.51	15	29/25	12.9	.19/1.0/4.0
26	Tb+Pd,Re/C	fixed bed	$TbCl_3$	.084/.147/.52	15	30/26	13	.56/1.0/4.0
27	Lu+Pd,Re/C	fixed bed	$LuCl_3*6H_2O$	.094/.147/.52	15	30/26	13	.63/1.0/4.0
28	Sc+Pd,Re/C	fixed bed	$ScCl_3*6H_2O$	.025/.147/.52	15	29/26	13	.16/.98/4.0
29	Nb+Pd,Re/C	fixed bed	$NbCl_5$	.044/.147/.50	15	30/25	12.6	.29/.98/4.0

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TABLE 2
CATALYST PERFORMANCE: BACK MIXED SLURRY REACTOR[1]

EX.	CATALYST	PREPARATION	THF STY	SELECTIVITY
31	Pd,Re/C	Ex. A	280	90
32	Rh+Pd,Re/C	Ex. 1	500	88-90
33	Ru+Pd,Re/C	Ex. 2	350	88-90
34	Co+Pd,Re/C	Ex. 3	430	90-92
35	Fe+Pd,Re/C	Ex. 4	413	90

1 Hydrogenation of 40% maleic acid at 250°C in excess flowing H_2, 2,000 psig total pressure.

TABLE 3
CATALYST PERFORMANCE: PLUG FLOW FIXED BED REACTOR[1]

EX.	CATALYST	PREP.	ACID CONV. (2)	SELEC-TIVITY (3)	THF STY
36	Pd,Re/C	EX. B	58(%) (4)	83(%)	389
37	Rh+Pd,Re/C	EX. 5	77.5	74	374
38	Ru+Pd,Re/C	EX. 6	72(4)	70	384
39	Co+Pd,Re/C	EX. 7	81.6(4)	85	484
40	Fe+Pd,Re/C	EX. 8	93.5	82	658
41	Pt+Pd,Re/C	EX. 11	75.2	76	432
42	Tm+Pd,Re/C	EX. 13	88	85	407
43	Ce+Pd,Re/C	EX. 14	91	81	537
44	Y+Pd,Re/C	EX. 15	88	85	383
45	Nd+Pd,Re/C	EX. 16	85	86	425
46	Al+Pd,Re/C	EX. 17	81	79	393
47	Pr+Pd/Re/C	EX. 18	86	85	461

	48	Ho+Pd,Re/C	EX. 19	83	85	404	
	49	Cu+Pd,Re/C	EX. 20	82	85	422	
	50	Sm+Pd,Re/C	EX. 21	81	84	355	
	51	Eu+Pd,Re/C	EX. 22	77	85	361	
5	52	Hf+Pd,Re/C	EX. 23	73	80	433	
	53	Mn+Pd,Re/C	EX. 12	74	83	370	
	54	V+Pd,Re/C	EX. 24	75	82	410	
	55	Cr+Pd,Re/C	EX. 25	84	81	390	
	56	Au+Pd,Re/C	EX. 10	67(4)	84	404	
10	57	Tb+Pd,Re/C	EX. 26	69	84	316	
	58	Lu+Pd,Re/C	EX. 27	72	83.5	304	
	59	Ni+Pd,Re/C	EX. 9	64	82	405	
	60	Sc+Pd,Re/C	EX. 28	77	84.5	482	
	61	Nb+Pd,Re/C	EX. 29	74	79	491	

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1 Hydrogenation of 5% maleic acid at 250°C in excess
  flowing H_2, 2,000 psig total pressure.

2 Percent (maleic+succinic) acids converted at contact
  time of 0.016 hour.

20 3 Maximum percent selectivity to (THF + BDO + GBL).

4 Percent (maleic+succinic) acids converted at
  contact time of 0.016 hour; determined by
  difference, not by titration.

TABLE 4

25   CATALYST PERFORMANCE VS.
      TEMPERATURE: PLUG-FLOW FIXED BED REACTOR[1]

EX.	CATALYST	PREPA-RATION	TEMP	ACID CONV (2)	SELEC-TIVITY (3)	THF STY
62	Pd,Re/C	B	250	90(%)	83(%)	391
63	Pd,Re/C	B	225	77	88	240
64	Pd,Re/C	B	275	89	76	493
65	Rh,Pd,Re/C	EX.30	250	98	80	368
66	Rh,Pd,Re/C	EX.30	250	100	80	388

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67	Rh,Pd,Re/C	EX.30	200	76	84	142
68	Pd+Re,Rh	EX.5	250	97	74	374
69	Pd+Rh,Re	EX.5	200	79	84	124

5   1 Hydrogenation of 5% maleic acid in excess flowing H_2,
        2,000 psig total pressure.

       2 Percent (maleic+succinic) acids converted at contact
        time of 0.03 hour; determined by difference, not by
        titration;

10   3 Maximum percent selectivity to (THF + BDO + GBL).

                              TABLE B
             CATALYST PERFORMANCE: BACKMIXED SLURRY REACTOR[1]

15

Example	Catalyst	Preparation	Acid Feed Rate[2]
70	K,Pd,Re/C	Ex.C	24 cc/hr
			32
			31

Example	Acid Conc[3]	THF STY	Selectivity THF+BDO+GBL
70	4.9%	285	85%
	6.4	355	85
	5.6	324	85

       1 Hydrogenation of 40% maleic acid at 250C in
        excess flowing H_2, 2,000 psig total pressure.
25   2 Feed rate of 40% maleic acid/water in cc/hr.
       3 Concentration of acid in the reactor, reported as
        weight % succinic acid, measured by acid-base
        titration.

30
       The beneficial effect of addition of potassium to the
       bimetallic Pd,Re/C catalyst are apparent- STY
       increased from 280 to approximately 335.

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CLAIMS

What is claimed:

1. A polymetallic catalytic composite
consisting essentially of a combination of a
catalytically effective amount of fine particles of a

      (a) palladium component;

      (b) rhenium component; and

      (c) one or more of a metal component

            selected from rhodium, cobalt, platinum,

            ruthenium, iron, thulium, cerium, yttrium,

            neodymium, aluminum, praesodymium and

            holmium

deposited on a support.

2. The polymetallic catalytic composite of
Claim 1 wherein the palladium component ranges from
about 0.1 to 10 weight percent, the rhenium component
ranges from about 1 to 20 weight percent and the metal
component ranges from about 0.01 to 1.0 weight percent
by total weight.

3. The polymetallic catalytic composite of
Claim 1 or Claim 2 wherein the support is selected
from the group consisting essentially of an activated,
porous carbon carrier having a surface area in excess
of 650 m^2/g or a refractory oxide carrier.

4. A hydrogenation catalyst consisting
essentially of a polymetallic catalytic composite of
fine particles of palladium, rhenium and one or more
of a metal component selected from rhodium, cobalt,
platinum, ruthenium, iron, thulium, cerium, yttrium,
neodymium, aluminum, praesodymium, holmium, copper,
samarium europium, hafnium, manganese, vanadium,

chromium, gold, terbium, lutetium, nickel, scandium
and niobium on an activated porous carbon support
having a surface area in excess of 650 m^2/g and
comprising about 0.1 to 10 weight percent of
5   palladium, about 1 to 20 weight percent of rhenium and
about 0.01 to 1.0 weight percent of the metal
component by total weight to achieve increased space
time yield of product while maintaining high
selectivity in a back mixed reactor or to achieve high
10   activity in a plug flow reactor.

          5.   The catalyst of Claim 4 wherein the
metal component is selected from rhodium, cobalt,
platinum, ruthenium, iron, thulium, cerium, yttrium,
15   neodymium, aluminum, praesodymium and holmium.

          6.   A process for preparing tetrahydrofuran
or substituted tetrahydrofuran from a hydrogenatable
precursor, the process comprising contacting the
20   hydrogenatable precursor with hydrogen at a
temperature of about 150°C to about 300°C, and a
pressure of about 1000 psig to about 3000 psig in the
presence of a polymetallic catalytic composite
comprising a combination of a catalytically effective
25   amount of fine particles of a
                (a) palladium component;
                (b) rhenium component; and
                (c) one or more of a metal component
                selected from rhodium, cobalt, platinum,
30   ruthenium, iron, thulium, cerium, yttrium,
                neodymium, aluminum, praesodymium, holmium,
                c oper, samarium, europium, hafnium,
                ma ganese, vanadium, chromium, gold,
                terᵢ·um, lutetium, nickel, scandium and
35   niobiuᵣ

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deposited on a support.

7.   The process of Claim 6 wherein the
hydrogentable precursor is selected from itaconic
acid, itaconic anhydride, citraconic acid, citraconic
anhydride, mesaconic acid, citric acid and aconitic
acid or mixtures thereof.

8.   The process of Claim 6 wherein the metal
component is selected from rhodium, cobalt, platinum,
ruthenium, iron, thulium, cerium, yttrium, neodymium,
aluminum, praesodymium and holmium.

9.   The process of Claim 6 or Claim 8
wherein the support is selected from the group
consisting of an activated, porous carbon carrier
having a surface area in excess of 650 m^2/g or a
refractory oxide carrier.

10.   The process of 9 wherein the palladium
component comprises about 0.1 to 10 weight percent,
the rhenium component comprises about 1 to 20 weight
percent and the metal component comprises about 0.01
to 1.0 weight percent of the total weight.

11.   The process of Claim 10 wherein the
hydrogenatable precursor is selected from the group
consisting of maleic acid, maleic anhydride, fumaric
acid, succinic acid, succinic anhydride, malic acid,
or mixtures thereof and is in an aqueous or organic
solvent medium.

a·

12.   The process of Claim 11 wherein the
hydrogenatable precursor is selected from maleic acid
and the solvent medium is water.

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13. A process for preparing tetrahydrofuran
from an aqueous solution of maleic acid to achieve
increased space time yield while maintaining high
selectivity or exhibiting high activity, the process
5   comprising contacting said maleic acid with hydrogen
at a temperature of about 150°C to about 300°C, and a
pressure of about 1000 psig to about 3000 psig in the
presence of a trimetallic catalytic composite
comprising a combination of fine particles of a
10   (a) about 0.9-1.0 weight percent palladium
                component;
                (b) about 2.1-4.5 weight percent rhenium
                component; and
                (c) about 0.1 -0.6 weight percent of a metal
15   component selected from rhodium, cobalt,
                platinum, ruthenium, iron, thulium, cerium,
                yttrium, neodymium, aluminum, praesodymium
                and holmium
deposited on an activated porous carbon support having
20   a surface area in excess of 650 m^2/g.

14. A process for preparing tetrahydrofuran
from a hydrogenatable precursor in a back-mixed
reactor, the process comprising contacting the
25   hydrogenatable precursor with hydrogen at a
temperature of about 150°C to about 300°C, and a
pressure of about 1000 psig to about 3000 psig in the
presence of a polymetallic catalytic composite
comprising a combination of a catalytically effective
30   amount of fine particles of a
                (a) palladium component;
                (b) rhenium component; and
                (c) one or more of a metal component
                selected from rhodium, cobalt, platinum,
35   ruthenium, iron, thulium cerium, yttrium,

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neodymium, aluminum, praesodymium, holmium,
copper, samarium, europium, hafnium,
manganese, vanadium, chromium, gold,
terbium, lutetium, nickel, scandium and
5   niobium
deposited on a support.

15.   A process for preparing tetrahydrofuran
from a hydrogenatable precursor in a plug flow
10   reactor, the process comprising contacting the
hydrogenatable precursor with hydrogen at a
temperature of about 150°C to about 300°C, and a
pressure of about 1000 psig to about 3000 psig in the
presence of a polymetallic catalytic composite
15   comprising a combination of a catalytically effective
amount of fine particles of a
            (a) palladium component;
            (b) rhenium component; and
            (c) one or more of a metal selected from one
20   or more of a metal component selected from
            rhodium, cobalt, platinum, ruthenium, iron,
            thulium, cerium, yttrium, neodymium,
            aluminum, praesodymium, holmium, copper,
            samarium, europium, hafnium, manganesium,
25   vanadium, chromium, gold, terbium, lutetium,
            nickel, scandium and niobium
deposited on a support.

16.   The process of Claim 14 or Claim 15
30   wherein the hydrogenatable precursor is selected from
the group consisting essentially of maleic acid,
maleic anhydride, fumaric acid, succinic acid,
succinic anhydride, maleic acid or mixtures thereof.

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17. The process of Claim 16 further including the hydrogenatable precursor in an aqueous or organic solvent medium.

5   18. The process in Claim 13 or Claim 14 or Claim 15 wherein the support is an activated, porous carbon carrier having a surface area in excess of 650 m^2/g or a refractory oxide carrier.

10   19. The process of Claim 14 further comprising an aqueous, continuous process wherein the hydrogenatable precursor is maleic acid and the concentration of carboxylic acids in the reaction mixture is 1% to 10% by weight of the reaction mixture
15   to accomplish high selectivity to tetrahydrofuran while minimizing over reduction of tetrahydrofuran.

20. An aqueous process for the manufacture of high purity tetrahydrofuran or substituted
20   tetrahydrofuran by the continuous hydrogenation with vapor take off of tetrahydrofuran of a hydrogenatable tetrahydrofuran precursor selected from the group consisting of maleic acid, maleic anhydride, fumaric acid, succinic acid, succinic anhydride, malic acid,
25   and mixtures thereof, and itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, citric acid, aconitic acid or mixtures thereof, in the presence of a suitable hydrogenation catalyst and maintaining the concentration of
30   carboxylic acids in the reaction mixture in a predetermined range.

21. The process of Clai~ 20 wherei₁ the precursor is selected from maleic acid or itacc ⁀ic
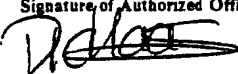35   acid.

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        22. The process of Claim 20 or Claim 21
wherein the suitable hydrogenation catalyst comprises
fine metallic particles on an activated porous carbon
  5   support comprising by total weight of from about 0.1
to 10 wt % of palladium, about 1 to 20 wt % of rhenium
and optionally from about 0.01 to 1.0 wt % of a metal
component selected from rhodium, cobalt, platinum,
ruthenium, iron, thulium, cerium, yttrium, neodymium,
 10   aluminum, praesodymium, holmium, copper, samarium,
europium, hafnium, manganesium, vanadium, chromium,
gold, terbium, lutetium, nickel, scandium and niobium.

        23. The process of Claim 19 or Claim 20 or
 15   Claim 21 wherein the concentration of acids is 3% to
8% by weight.

        24. The process of Claim 19 or Claim 20
wherein the catalyst is of Claim 4 and the support is
 20   an activated porous carbon carrier having a surface
area in excess of 1000 m^2/g.

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INTERNATIONAL SEARCH REPORT

International Applic   a No   __PCT/US 91/05165__

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[b]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl.5   B 01 J 23/89   B 01 J 23/64   C 07 D 307/08

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl.5	B 01 J C 07 D

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[o]	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
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X	US,A,4795733 (DE THOMAS) 3 January 1989, see column 8; claims 1,2 see column 6; example 1	1,4,5
X	US,A,4302359 (C. MAULDIN) 24 November 1981, see column 10; claims 1,6; column7; example A; column 4, line 42 – column 5, line 14	1,2
Y		3,6-22, 24
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* Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other su   documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
07-11-1991	5. 12. 91

International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	Danielle van der Haas

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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The members are as contained in the European Patent Office EDP file on 25/11/91
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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